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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

REQUEST FOR FILING REISSUE PATENT APPLICATION

The Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

This is a request for a reissue patent application of:

Inventor: Mendicino et al.

Title: SURFACE-ACTIVE ADDITIVES IN THE DIRECT SYNTHESIS OF
TRIALKOXYSILANES

Patent No: 5,783,720 **Issue Date:** July 21, 1998

Serial No.: 08/729,266 **Filing Date:** October 10, 1996

Date of this reissue application filing: January 20, 2000

Attorney docket no: Witco-103

This application for reissue includes:

☒ Specification: 26 pages (only spec. and claims)
☒ Abstract: 1 page(s)
☐ Drawings: 1 sheet(s) per set:
 ___1___ set(s) informal;
 ___ set(s) formal of size ___A4 ___ 13" ___ 14"

☒ Declaration
☒ Assent of Assignee
☐ Request for Title Search
☐ Verified Statement establishing small entity status
☒ Power of Attorney (included in Declaration)
☒ Also attached:
 (1) letter requesting transfer of formal drawings
 (2) Form PTO-1449
 (3) copies of 38 references cited



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Fee Calculation:

Basic Filing Fee (\$690/\$345) \$ 690

Claim fees:

	<u>Claims in</u> <u>reissue app.</u>	<u>Claims in</u> <u>orig. patent</u>	
Total effective claims	(A) 23	(B) 18	(A) minus [larger of (B) or 20] = <u>5</u> x \$18/\$9= \$ 90

Total indep. claims	(D) 1	(E) 1	(D) minus (E) = <u>0</u> x \$78/\$39= \$ 0
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Title Search Fee (\$25.00) \$

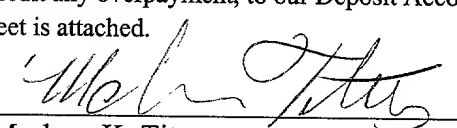
Petition Fee per Rule 27(h) for Rule 47 Petition (\$130.00) \$

Other Fees: \$

TOTAL FEES ENCLOSED \$ 780

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Submitted by:


Marlana K. Titus

Reg. No. 35,843

Tel. No. (301) 924-9600

Fax. No. (301) 924-5883

Nash & Titus, LLC
3415 Brookeville Road
Suite 1000
Brookeville, Maryland 20833

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CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)Applicant(s): **MENDICINO et al.**

Docket No.

WITCO-103

Serial No.

08/729,266

Filing Date

October 10, 1996

Examiner

Paul Shaver

Group Art Unit

1204Invention: **SURFACE-ACTIVE ADDITIVES IN THE DIRECT SYNTHESIS OF TRIALKOXY-SILANES**

I hereby certify that this **Reissue application, Declaration, Assent of Assignee, IDS, and all accompanying papers**
(Identify type of correspondence)

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under
37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 on
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IN RE THE
APPLICATION OF

MENDICINO ET AL.

FOR REISSUE LETTERS PATENT OF
UNITED STATES PATENT NO. 5,783,720

FOR

“SURFACE-ACTIVE ADDITIVES IN THE DIRECT
SYNTHESIS OF TRIALKOXY-SILANES”

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United States Patent [19]

Mendicino et al.

[54] **SURFACE-ACTIVE ADDITIVES IN THE
DIRECT SYNTHESIS OF
TRIALKOXYSILANES**

[75] **Inventors:** Frank D. Mendicino, Marietta;
Thomas E. Childress, Newport, both
of Ohio; Sebastiano Magri, Asia, Italy;
Kenrick M. Lewis, Rego Park; Hua
Yu, White Plains, both of N.Y.

[73] **Assignee:** OSi Specialties, Inc., Greenwich, Conn.

[21] **Appl. No.:** 729,266

[22] **Filed:** Oct. 10, 1996

[51] **Int. Cl.⁶** C07F 7/04; C07F 7/18

[52] **U.S. Cl.** 556/470

[58] **Field of Search** 512/470

[45] **Date of Patent:** Jul. 21, 1998

U.S. PATENT DOCUMENTS

4.113.761	9/1978	Kreuzburg et al.	556/470
4.931.578	6/1990	Ohta et al.	556/470
5.362.897	11/1994	Harada et al.	556/470

Attorney, Agent, or Firm—Scully, Scott, Murphy & Presser

Disclosed is a process in which surface-active additives are used in the slurry phase Direct Synthesis of trialkoxysilanes to shorten the period between the start of the reaction and the attainment of steady-state rates and selectivities, to improve product yields and to control or prevent foam formation. Compositions comprising silicone antifoam compounds and fluorosilicone polymers are the preferred surface-active additives of the instant process.

18 Claims, 1 Drawing Sheet

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U.S. Pat. No. 4,727,173 discloses that the use of copper (II) hydroxide as catalyst avoids the limitations associated with cuprous chloride and provides a high selectivity to trialkoxysilanes. The preferred solvents are diphenyl ether, polyaromatic hydrocarbons like THERMINOL® 59, THERMINOL® 60 and THERMINOL® 66, and alkylated benzenes such as dodecylbenzene. However, when copper (II) hydroxide is used in combination with alkylated benzene solvents, such as dodecylbenzene, the Direct Synthesis of trialkoxysilanes becomes unstable after approximately 25–35 weight percent of the silicon has been reacted. When methanol is the alcohol reactant at temperatures above about 220° C., the trimethoxysilane content in the reaction product declines from approximately 90–95 weight percent to approximately 50–60 weight percent and recovers again to between 80–95 weight percent after about 60 percent silicon conversion. Simultaneous with this loss of selectivity is the enhanced formation of methane, water and dimethyl ether. Methane and dimethyl ether formation represent inefficient use of the methanol reagent. Problems attendant to the generation of water in the reaction mixture have been recited hereinabove.

U.S. Pat. No. 5,527,937 (European Patent application EP 0709388 A1) discloses a process for the Direct Synthesis of triethoxysilane and trimethoxysilane, wherein CuCl is the catalyst, tri- and tetra- toluenes and/or their alkyl substituted derivatives are the solvents and dimethylsilicone oils are antifoaming agents. The polyphenyl solvents of this process are expensive heat transfer fluids.

Thermal activation of slurries containing copper catalysts and silicon is disclosed in a number of patents, for example, U.S. Pat. Nos. 3,775,457 and 4,727,173. Use of hydrogen to activate silicon with copper for the Direct Reaction has been disclosed in U.S. Pat. Nos. 2,380,997; 2,473,260; 3,641,077; and 4,314,908. Hydrogen activation, as taught in these patents, is accomplished at temperatures above about 400° C. in fixed bed reactors, fluidized bed reactors or furnaces

with silicon—copper catalyst mixtures containing more than 1.5 weight percent copper. No teaching is given regarding selectivity, reactivity and reaction stability of the silicon—copper masses in the slurry phase Direct Synthesis of trialkoxysilanes.

Suzuki, et al. (Bulletin of the Chemical Society of Japan, vol. 64 (1991) pp 3445–3447) disclosed that hydrogen activation of silicon— CuCl_2 mixtures (2.5 wt % Cu) in a fixed bed at 260°C . afforded complete silicon conversion and high (89%) selectivity to trimethoxysilane in a fixed bed Direct Reaction with methanol. The duration of the induction period, the reaction rate and selectivity to trimethoxysilane were all very dependent on the temperature of hydrogen activation.

Thus, there continues to exist the need for a stable, highly selective and rapid Direct Synthesis of trialkoxysilanes which is conducted in cheaper, less hazardous solvents and yet avoids the above-mentioned deficiencies of copper chlorides and alkylated benzenes. In particular, there is a need for such a Direct Synthesis which eliminates or avoids the alcohol reduction and alcohol dehydration side reactions. These needs are addressed in a copending patent application filed on even date herewith and assigned to the assignee of the present application, bearing internal file number 89603 and entitled "Activation of Copper-Silicon Slurries for the Direct Synthesis of Trialkoxysilanes".

There is also a need for a Direct trialkoxysilane Synthesis process in which foaming is controlled so that the reaction slurry is retained in the reactor. Moreover, the foam control method(s) must not have any deleterious effect(s) on the selectivity, rate and stability of the Direct Synthesis of trialkoxysilanes and must remain effective throughout the entire course of the reaction, especially when the solvent is used for more than one charge of silicon, when recycled solvent is used, or when the Direct Process is conducted continuously.

OBJECTS OF THE INVENTION

It is therefore an object of the invention to provide a process for producing trialkoxysilane directly from silicon metal and alcohol which results in a high trialkoxysilane to tetraalkoxysilane ratio in the product over the entire course of the reaction.

Another object of the invention is to provide such a highly selective process while avoiding foaming and its attendant problems.

Another object of the invention is to provide such a Direct Synthesis process which results in a high conversion of silicon metal into trialkoxysilane product and which results in little unreacted silicon content in the solid reaction residue.

A still further object is to provide such a Direct Synthesis process in which there is only a short delay between the start of the reaction and the attainment of high, stable reaction rates and selectivities.

A further object of the invention is to provide such a Direct Synthesis process which does not require the use of costly corrosion resistant materials in the construction of the process apparatus.

SUMMARY OF THE INVENTION

The present invention provides a process for producing trialkoxysilane of the formula $\text{HSi}(\text{OR})_3$, wherein R is an alkyl group containing from 1 to 6 carbon atoms inclusive, which process comprises:

(a) slurring silicon metal in a thermally stable solvent, preferably an alkylated benzene or polyaromatic hydrocarbon solvent, in the presence of a catalytically effective amount of a copper catalyst precursor and of a surface-active additive hereinafter defined and, optionally, an alcohol of formula ROH; (b) activating said catalyst precursor, for instance by heating and agitating this slurry, and/or optionally injecting into it nitrogen and/or other inert gas, and/or injecting into the slurry a reducing agent such as hydrogen, carbon monoxide or monosilane or reducing gases containing them, to reduce non-zerovalent copper present to zerovalent copper, to produce a copper-activated silicon slurry; (c) reacting this copper-activated silicon slurry with an alcohol of the formula ROH to produce said trialkoxysilane; and (d) recovering said trialkoxysilane from the reaction product.

The present process prevents significant foam formation and affords good reaction stability. The surface-active agents used for foam control also effect a reduction in the time from the start of the reaction to the attainment of stable rates and selectivities. The process produces trialkoxysilanes at high rates and in quantity such that the gravimetric ratio of trialkoxysilane to tetraalkoxysilanes are greater than about 9 to 1 when calculated over the entire course of the reaction. Furthermore, the use of copper catalyst precursor as defined herein, hydrogen and the organosilicone and/or fluorosilicone surface-active additives does not generate corrosive materials and, thus costly materials of construction are not required for the reactor. The process of the invention also results in high overall conversion of silicon and alcohol to desirable products.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flowsheet of a useful embodiment of the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The following equations are representations of the principal chemical reactions occurring during the Direct Synthesis of trialkoxysilanes.



The desirable products of the instant Direct Synthesis are trialkoxysilanes of general formula, $\text{HSi}(\text{OR})_3$, wherein R is an alkyl group of 1 to 6 carbon atoms. R is preferably methyl and ethyl. Byproducts of the synthesis are $\text{Si}(\text{OR})_4$, $\text{RSiH}(\text{OR})_2$, $\text{RSi}(\text{OR})_3$, linear, branched and cyclic silicates such as $(\text{RO})_3\text{SiOSi}(\text{OR})_3$, $\text{H}(\text{RO})_2\text{SiOSi}(\text{OR})_2\text{H}$, $\text{HSi}(\text{RO})_2\text{SiOSi}(\text{OR})_3$, $(\text{R}(\text{O}))_3\text{SiOSi}(\text{OR})_2\text{R}$, $(\text{RO})_3\text{SiOSi}(\text{RO})_2\text{OSi}(\text{RO})_3$, $(\text{RO})_3\text{SiOSi}(\text{OR})\text{HOSi}(\text{OR})_3$, $(\text{RO})_3\text{SiOSi}(\text{OR})\text{ROSi}(\text{OR})_3$, $(\text{RO})\text{Si}[\text{OSi}(\text{OR})_3]_3$, $(\text{RO})_3\text{SiOSi}(\text{OR})(\text{OSi}(\text{RO})_3)\text{OSi}(\text{OR})_3$, and $[\text{OSi}(\text{OR})_2]_n$, (n4, 5 . . .), hydrogen gas, hydrocarbons (RH) such as methane and ethane, alk-

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CATALYST PRECURSORS

Copper and halogen-free copper compounds which are readily reduced to copper by hydrogen, alcohols, organosilanes containing SiH, SiH₂ or SiH₃ groups, monosilane, carbon monoxide and/or heating in polyaromatic hydrocarbons, are useful as catalyst precursors of this inventive process. Suitable examples are metallic copper powders, including those produced by supercritical processes and metal atom vaporization, or in situ in the reaction slurry of the Direct Synthesis, copper colloids, copper oxides, copper hydroxides, mixed hydrous oxides such as 3CuO.Cu(OH)₂, copper alkoxides (typically of the formula Cu(OA)₁₋₂ wherein A is alkyl containing 1 to 6 carbon atoms, for example, Cu(OCH₃)₂, Cu(O-tC₄H₉) and carboxylates (typically of the formula Cu(OOA)₁₋₂ wherein A is as defined herein, for example, Cu(OOCH)₂, Cu(OOCCH₃)₂). All polymorphic forms of copper (II) hydroxide, particularly the cubic and orthorhombic polymorphs, are preferred catalyst precursors of the instant invention.

The copper catalyst precursor used in the process of this invention is present in an amount effective to catalyze the reaction upon activation. Generally an effective amount ranges from about 0.01 to about 5 parts by weight of catalyst precursor per 100 parts by weight of the silicon metal. Usually the amount of catalyst precursor will be from about 0.1 to about 2.6 parts by weight per 100 parts by of the weight silicon metal. The preferred amount of copper catalyst precursor is from about 0.1 to about 1.0 parts by weight per 100 parts by weight silicon metal.

Copper (II) hydroxide used in the present invention is preferably anhydrous, but material containing water of hydration is also usable. The water content of commercial copper (II) hydroxide may be as high as 20 weight percent. If a hydrated catalyst precursor is used, provision must be made in the design of the apparatus to avoid contact of the water formed during its reduction and thermal decomposition with the trialkoxysilane reaction product.

In addition to water content, various other criteria can be used to characterize the copper catalysts and catalyst precursors of this invention. Surface area of the catalyst precursor can be as low as 0.1 m²/g. Areas in the range 10-50 m²/g are preferred. Particle size of the copper catalyst precursor can be from less than 1 micron up to about 100 microns. The desirable range is 0.1-50 microns and the preferred range 0.1-30 microns.

The presence of excessive tin in the reaction has adverse effects on the reaction rate and/or the selectivity for trialkoxysilane and so such excessive tin levels should be avoided. It is desirable that the tin content of the catalyst precursor (and the catalyst itself) be less than 1000 parts per million, preferable that it be less than 300 parts per million and most preferable that it be less than 100 parts per million. Gravimetry and atomic absorption spectroscopy are suitable methods for quantifying the silicon content of the reaction solvent. Analytical procedures are published, for example, in *The Analytical Chemistry of Silicones*, (A. L. Smith, Editor), John Wiley & Sons Inc., NY, 1991, chapter 8. Soluble silicates retained in the reaction solvent are a measure of the extent to which side reactions such as those in equations 6-8 have occurred. All of these reactions depend on the presence of water, which is formed, for example, by the reaction of Equations [3-5]. Gels and soluble silicates contained in the reaction solvent can be removed with boric acid and borates according to the method disclosed by Bailey, et al. in U.S. Pat. No. 5,166,384, which is hereby incorporated by reference.

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Of greater importance is the tin content of the reaction slurry. Based on the weight of silicon at the outset of a reaction, it is desirable that the tin content be less than 100 parts per million and preferable that it be less than 10 parts per million.

Zinc content of the catalyst precursor is desirably less than 2500 parts per million and preferably less than 1500 parts per million. Based on the initial weight of silicon charged to the reactor, the zinc content of the reaction slurry must be less than 100 parts per million, and preferably less than 50 parts per million. Other critical trace elements which are ordinarily contained in the catalyst precursor are lead (Pb) and chloride (Cl^-). Their concentrations in the slurry must be <50 parts per million and <100 parts per million, respectively. We have determined that copper halide compounds such as CuCl and CuCl_2 are effective catalyst sources when employed with the surface-active agents in the process of this invention. The chloride restriction above arises not from catalytic inefficiency or ineffectiveness, but from its impact on reactor corrosion.

SILICON

The silicon metal reactant used in the process of this invention can generally be any commercially available grade of silicon in particulate form. It may be produced by any of the methods in current practice such as casting, water granulation, atomization and acid leaching. These methods are more fully described in *Silicon for the Chemical Industry*, vols. I, II III, (H. Oye, et al. Editors), Tapir Publishers, Norwegian Institute of Technology. A typical composition of commercial silicon metal useful in this invention expressed in percent by weight, is Si-98.5%, Fe<1%, Al-0.05 to 0.7%, Ca-0.001 to 0.1%; Pb<0.001%, Water<0.1%. Generally, smaller particle sizes are preferred for ease of dispersion in the slurry, faster reaction and minimization of erosion in the reactor. Sieving of ground silicon to regulate particle size is optional. An unsieved sample with particle sizes from <45 microns to >600 microns performed as satisfactorily as a sieved one with particle sizes in the narrower range of 75-300 microns.

ALCOHOL

The alcohols which are useful in the process of this invention are those of the formula ROH wherein R is an alkyl group containing from 1 to 6 carbon atoms, inclusive. Preferably R is an alkyl group containing from 1 to 3 carbon atoms inclusive. The most preferred alcohols are methanol and ethanol. While it is customary to use a single alcohol in the Direct Process, mixtures of two or more may also be used to prepare trialkoxysilanes with different alkoxy groups, or to facilitate the reaction of a less reactive alcohol. For example, about 5 weight percent methanol may be added to ethanol to improve the rate and stability of the Direct Synthesis of triethoxysilane. Alternatively, reaction may be initiated with one alcohol and continued with another, or with a mixture. Thus, a hydrogen activated slurry may be reacted initially with methanol prior to the Direct Reaction with ethanol.

Generally, the reaction is run batchwise in a slurry and the alcohol is fed into the slurry as a gas or liquid. Gaseous introduction is preferred. An induction period lasting from a few minutes up to about five hours may be observed. The initial alcohol feed rate is optionally controlled at a low level and increased following the induction period. Similarly, the alcohol feed rate is optionally reduced after about 70 weight percent silicon conversion to minimize the formation of

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SOLVENT

Silicon metal, catalyst, surface-active additive and solvent can be added together in the reactor in any order. The solvent is present in an amount sufficient to disperse the solid and gaseous reactants homogeneously. Generally, reactions are initiated with solvent and solids in a gravimetric ratio between 1:2 and 4:1, preferably 1:1 to 2:1. However, as the silicon is consumed during batchwise Direct Synthesis, the solvent to solids ratio will increase. The ratio can be maintained within narrow limits of the preferred range for continuous reactions.

The surface-active additives of the instant invention are compositions comprising hydrophobized solids (usually

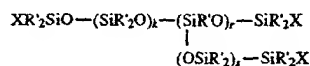
$$\begin{array}{c} \text{R}^n_3\text{SiO}-(\text{SiR}^{n-2}\text{O})_k-(\text{SiR}^n\text{O})_l-\text{SiR}^n_3 \\ | \\ (\text{OSiR}^{n-2})_m-\text{SiR}^n_3 \end{array}$$

Suitable examples for use with the instant invention include the OSi Specialties products, SAG® 47, SAG® 100 and SAG® 1000. These may be mixed with the reaction solvent, or another thermally stable carrier, prior to addition to the reaction slurry. Under Direct Synthesis conditions, the effective quantities depend on factors such as the alcohol feed rate, the specific alcohol employed, the reactor pressure, the specific solvent, the concentration of con-

densified silicates in the slurry and the intrinsic antifoaming properties of the antifoam compound. For example, more foam is generated at higher alcohol feed rates than at lower values. Usually, foaming becomes evident in the first few minutes after alcohol injection and, later after the reaction has been in progress for some time, when the soluble silicate concentration has increased beyond a threshold level. An increase of reactor pressure (from atmospheric up to 2 atmospheres) will sometimes temporarily collapse the foam. However, since the Direct Synthesis performance is higher at lower pressures, this mechanical approach is not desirable. The discharge of foaming reaction slurry from the reactor may be avoided by increasing the freeboard (disengagement height) above the liquid level in the reactor. However, this means loss of maximum reactor capacity. Thus, effective and durable use levels can range from 0.0001–5 weight percent, depending on the specific anti-foam compound used. These percentages are calculated based on the total weight of slurry (solvent, silicon and catalyst precursor) charged to the reactor.

Organofluoropolysiloxanes (fluorosilicones) useful in the present invention contain one or more carbon—fluorine bonds, typically at least two carbon atoms away from the carbon atom bonded directly to silicon. A review of organofluorosiloxane chemistry and applications has been published by B. Boutevin and Y. Pietrasanta in *Progress in Organic Coatings*, vol. 13 (1985) pp 297–331.

The organofluoropolysiloxanes of this invention may be linear oligomers and polymers of general formulae: $XR'_2SiO—(SiR'_2O)_k—SiR'_2X$ or cyclic oligomers of general formula: $(R'_2SiO)_n$, or branched oligomers and polymers of the type:



in which each R' group is the same different and each is a monovalent hydrocarbon group as defined above for R" groups, provided that at least one R' group is partially or completely substituted with fluorine so as to be a fluorocarbon group. X has the same meaning as R' or is optionally an alkoxy group containing eight or fewer carbon atoms and k, r and s are positive numbers and n is an integer greater than 3. The values of k, n, r and s are chosen such that the fluorosilicone has a normal boiling point that is at least 10° C. higher than the temperature of the Direct Synthesis slurry. In a particular composition, all of the R' groups may be fluorocarbon, or some may be fluorocarbon and the remainder hydrocarbon. The organofluoropolysiloxanes can be used as such, or in foam control compositions containing hydrophobized solids. Suitable organofluoropolysiloxanes include trialkylsilyl endcapped polytrifluoropropylmethylpolysiloxanes with viscosities in the range, 10–60,000 centipoise at 25° C., poly(dimethylsiloxane-co-trifluoropropylmethylsiloxanes) in the same viscosity range. FS 1265, a commercial fluorosiloxane polymer of this structural class having a viscosity of 1000 centipoise at 25° C., is a preferred surface-active additive of this invention.

Other examples of suitable fluorosiloxanes include $(C_8F_{17}C_3H_6SiCH_3O)_n$ ($n \geq 4$), $(CH_3)_3SiO(C_6F_9C_2H_4SiCH_3O)_{30}(Si(CH_3)_2O)_{200}Si(CH_3)_3$ and $C_2F_5C_2H_4Si(C_6H_5)_2O(Si(CH_3)_2O)_{100}(SiCH_2C_2H_4C_2F_5O)_5Si(C_6H_5)_2C_2H_4C_2F_5$. Effective use levels of the fluorosiloxane surface-active additives are in the range, 0.00001–5 weight percent, preferably 0.001–0.5 weight percent, based on the total initial weight of the reaction slurry.

ACTIVATION CONDITIONS

Activation is the process of incorporating catalyst, and if desired, other auxiliary agents, into the silicon to make it

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Polyaromatic hydrocarbons, for example those described hereinabove as solvents and heat transfer fluids, have been found to be suitable reducing agents for the catalyst precursors of this invention. Reduction of the catalyst precursor, or

its mixture with silicon, is carried out in a slurry reactor at temperatures below the boiling point of the polyaromatic hydrocarbon, which is then separated from the solids prior to the Direct Synthesis in alkylated benzene solvents. Following separation, the recovered polyaromatic hydrocarbon can be used again in subsequent reductive activations.

Activation of silicon-copper catalyst precursor mixtures with carbon monoxide (CO) or monosilane (SiH_4) is conducted in the same manner as described above for hydrogen. Appropriate safety precautions must be followed in handling SiH_4 on account of its pyrophoricity.

The use of hydrogen, carbon monoxide, monosilane and/or polyaromatic hydrocarbons to activate slurries at temperatures below 400°C . is disclosed in a patent application assigned to the assignee of the present application and filed on even date herewith, under internal file number 89603 entitled "Activation of Copper-Silicon Slurries for the Direct Synthesis of Trialkoxysilanes", which is hereby incorporated herein by reference.

REACTION CONDITIONS

Designs, descriptions and operational considerations pertinent to three phase reactors are contained in the following monograph, articles and patents:

A. Ramachandran and R. V. Chaudhari, Three Phase Catalytic Reactors, Gordon and Breach Science Publishers, NY, 1983

N. Gartsman, et al., International Chemical Engineering, vol. 17 (1977) pp 697-702

H. Ying, et al., Industrial & Engineering Chemistry, Process Design & Development, vol. 19 (1980) pp 635-638

N. Satterfield, et al., Chemical Engineering Science, vol. 35 (1980) pp 195-202

M. Boxall, et al., Journal of Metals, (August 1984) pp 58-61

Roeckel, C. Scaccia and J. Conti, U.S. Pat. No. 4,328,175 (May 4, 1982)

M. Litz, U.S. Pat. No. 4,454,077 (Jun. 12, 1984)

Reactors may be operated in a batchwise or continuous mode. In batchwise operation, a single addition of silicon and copper catalyst is made to the reactor at the outset and alcohol is added continuously, or intermittently, until the silicon is fully reacted, or reacted to a desired degree of conversion. In continuous operation, silicon and copper catalyst are added to the reactor initially and thereafter to maintain the solids content of the slurry within desired limits. The batchwise mode is illustrated in U.S. Pat. No. 4,727,173 and the continuous mode in U.S. Pat. No. 5,084,590. Both of these patents are incorporated herein by reference.

In its preferred form in accordance with the present invention, the Direct Synthesis of trialkoxysilanes is conducted in a continuously agitated slurry reactor with an activated silicon-copper catalyst mixture containing a surface-active ingredient capable of controlling foam formation and shortening the interval between onset of the reaction and the attainment of steady-state performance. The reactor may have a single nozzle or multiple nozzles for the introduction of gaseous alcohol. A means of continuous or intermittent addition of activated silicon-copper catalyst mixture, or of silicon, or of surface-active additive is also provided. Means for continuous removal and recovery of the volatile reaction products and unreacted alcohol are also desirably provided. Separation and purification of the trialkoxysilane products are optimally performed in the man-

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ner disclosed in U.S. Pat. No. 4,761,492 or U.S. Pat. No. 4,999,446, both of which are incorporated herein by reference.

When the initial loading of silicon and copper catalyst precursor is activated thermally in the reaction solvent or with a reducing gas such as hydrogen, carbon monoxide or monosilane in the presence of a surface-active additive according to the method of the instant invention, continuous slurry phase Direct Synthesis of trialkoxysilanes is advantageously continued by adding only silicon, or silicon containing less copper catalyst than that initially added, and optionally additional surface-active additive. In this way, the copper concentration of the slurry is controlled to minimize the transformation of the alcohol to hydrocarbons and water (Equations 3 and 5 above). Disadvantages caused by water have been recited hereinabove. Foam formation and the time to optimum stable, productivity and selectivity are also minimized.

The reaction is generally conducted at temperatures above about 150° C., but below such a temperature as would degrade or decompose the alcohols or solvents. Preferably, the reaction temperature is maintained in a range from about 200° C. to about 260° C. The reaction of methanol with the copper-activated silicon of the present invention is preferably operated at 220°–250° C., whereas the reaction of ethanol is preferably operated at 200°–240° C. The pressure at which the reaction is conducted is not critical and can be varied from subatmospheric to superatmospheric. Atmospheric pressure is generally employed.

Preferably, the contents of the reaction mixture are agitated to maintain a well mixed slurry of the copper-activated silicon particles and gaseous alcohol in the solvent. The reaction mixture is preferably well insulated to assure that the trialkoxysilane does not reflux. Refluxing can encourage the consecutive reaction of the trialkoxysilane with the alcohol, resulting in loss of the desired trialkoxysilane product by the formation of the tetraalkoxysilane.

At constant temperature, the reaction rate depends on the surface area and particle size of the silicon and on the feed rate of the alcohol. Higher rates are obtained at higher surface areas, finer particle sizes and higher feed rates. These parameters are selected so that a safe, economically sustainable product output is realized without endangerment to people, property and the environment. For example, silicon of 25–75 μ can be used to minimize side reactions and obtain high rates and selectivity to $\text{HSi}(\text{OC}_2\text{H}_5)_3$ at about 230° C., in place of 100–400 μ silicon at about 250° C.

Foaming can be detected visually in glass reactors, or through a sight glass (observation window) in commercial and pilot scale equipment. Occasionally, the first evidence of foaming is the partial or complete transfer of the reaction slurry to the product collection vessel. However, foaming can be detected in opaque equipment by, for example, monitoring the temperature in the line leaving the reactor with well spaced thermocouples. A rapid temperature increase in the outlet line from the reactor is indicative of foaming. Conversely, subsidence of the temperature indicates loss of foam height. It is desirable to operate the reactor with no, or controllably little, foam formation.

PERFORMANCE ADVANTAGES

In accordance with the present invention, the following substantial advantages are realized in the Direct Synthesis of trialkoxysilanes when surface-active additives are present in the reaction slurries.

Shortening of the period between the start of the reaction and the attainment of steady-state rates and selectivi-

ties. This leads to an improvement in the yield of trialkoxysilanes and more efficient use of raw materials.

Durable defoaming and antifoaming in the reaction slurries, especially those comprising recycled solvent containing soluble silicates from previous reactions. This leads to more controllable processes and more efficient use of reactor capacity.

DESCRIPTION OF FIG. 1

A schematic drawing of this reactor and its ancillary equipment is shown in FIG. 1. Alcohol is delivered from the reservoir (1) via the pump (2), flow meter (3) and vaporizer (4) to the reactor (5). Separate coils for methanol and the recycle stream are contained within the vaporizer. The reactor contains silicon and copper catalyst precursor suspended and dispersed in a high boiling solvent. A foam control agent is present. Provision is made for nitrogen injection upstream of the vaporizer and hydrogen injection downstream of the vaporizer as shown in the Figure. Alcohol reacts with the copper-activated silicon in the reactor. The reactor is fitted with a hopper (6) for solids, an agitator (7), heater and temperature controller (8), thermocouple bundle (9), internal baffles (10), spargers (11), pressure gauge (12) and pressure release safety valve (13). The gaseous reaction mixture leaves the reactor via the entrainment separator (14). Valve (15) permits sampling of the reaction mixture and venting of water vapor during the hydrogen activation step. (16) is an assembly of distillation columns adequate for the separation of unreacted alcohol and lower boilers from the desired trialkoxysilane. The columns are connected to a reboiler (17) and reflux condenser (18). Liquid reaction product (19) containing the desired trialkoxysilane and byproducts with higher boiling points is discharged from the unit to storage containers via the pump (20). The temperatures of the columns and reboiler are controlled such that stream (21) contains the byproduct gases, unreacted alcohol, alkoxysilanes and azeotropes boiling lower than the desired trialkoxysilane. A portion (22) of the liquid overhead stream is returned to the distillation columns as reflux flow. The remainder (23) is recycled through the vaporizer and re-injected into the reactor so that its contained alcohol can be reacted with copper—activated silicon. The vent gas stream (24) is admitted into a flowmeter capable of measuring total gas flow.

EXAMPLES

The following Examples illustrate the preferred embodiments of the instant invention. These are not intended to limit the scope of the invention. Rather, they are presented merely to facilitate the practice of the invention by those of ordinary skill in the art.

ABBREVIATIONS AND UNITS USED

Abbreviations used in the presentation of the data of the illustrative examples are the following:

ABBREVIATION	MEANING	ABBREVIATION	MEANING
TMS	$\text{HSi}(\text{OCH}_3)_3$	g	gram
TTMS	$\text{Si}(\text{OCH}_3)_4$	kg	kilogram
TES	$\text{HSi}(\text{OC}_2\text{H}_5)_3$	L	liters
SEL	$\text{HSi}(\text{OR})_3/\text{Si}(\text{OR})_4$	micron	
% Si/hr	percent silicon	m^2/g	square meters per

-continued

ABBREVIATION	MEANING	ABBREVIATION	MEANING
N600L	converted per hour		gram
N550BL	Nalkylene @ 600L	rpm	revolutions per minute
TH59	Nalkylene @ 550BL	wt %	weight percent
	Therminol @ 59	mm	minute

EQUIPMENT USED

Two laboratory scale Chemineer® reactors of similar design were used in the experiments illustrated hereinbelow. One had a capacity of 3.8 L and the other 5.8 L. A detailed description is given of the 5.8 L reactor and its ancillary equipment. Pilot scale experiments were conducted in a 400 L stainless steel reactor scaled to have the same energy input/volume ratio as the 5.8 L one.

The 5.8 L Chemineer® reactor had four 90° spaced, 1.27 cm wide baffles affixed to its wall. Agitation was provided by two stirrers attached to an axial shaft. The bottom one was a six blade turbine, 6.35 cm in diameter. A four blade propeller of the same diameter was placed 10 cm above the turbine. Power for agitation was provided by a variable speed air-driven motor whose rotational speed was measured by a magnetic tachometer. An electric heating mantle controlled by a heater/temperature controller was used to heat the reactor.

Methanol or ethanol was supplied to the reactor from a 1 L storage container via a calibrated FMI laboratory pump. Coiled stainless steel tubing, 0.32 cm internal diameter×305 cm length, placed in a 4 L silicone oil bath controlled at 150° C. served as the alcohol vaporizer. A similar vaporizer coil was available for the recycle stream, but it was not used during the course of these experiments. The alcohol inlet line entered through the top of the reactor. It was heat traced to prevent condensation of the vapor. Alcohol vapor was injected 2.5 cm from the bottom of the reactor and below the level of the six-blade turbine through a single downward pointing (0.63 cm internal diameter) sparger. A pressure gauge attached the alcohol vapor inlet line gave higher readings (up to about 2 atmospheres) when the sparger was plugged. Ordinarily, the gauge was at zero. Additional alcohol was supplied to the storage container during an experiment to maintain an uninterrupted flow of this reagent.

Reaction products and unreacted alcohol exited the reactor through a 91.4 cm×2.54 cm internal diameter packed tube, which served as entrainment separator and partial distillation column to remove solvent and higher boiling silicates from the product stream. The packing was ceramic saddles and stainless steel mesh. Five thermocouples were distributed along the length of the tube to record temperatures and warn indicate foaming. The lowest thermocouple was flush with the top of the reactor. As was indicated hereinabove, foaming was controlled by the use of FS 1265 and SAG® 100. Flexible tubing connected the outlet of the entrainment separator/partial distillation column to the four-way valve (15 in FIG. 1).

Two ten plate Oldershaw distillation columns served to separate the liquid reaction products and unreacted alcohol from the gases. Effluent from the reactor was admitted into the top of the lower column, which was attached at its lower end to a 3 neck 2 L round bottom flask supported in a heating mantle. The upper column was capped by a magnetically controlled reflux condenser and distillation head with thermocouple. The reflux condenser and another condenser

downstream were cooled to -25°C . by circulating silicone oil. Uncondensed gases exited the condenser through a vapor lock bubbler into the total gas flow meter (Model DTM-115, American Meter Co.). Wider tubing was employed downstream of the bubbler to avoid backpressures likely to shatter the glassware (columns, condensers and bubbler) or cause leaks at the joints. A gas sampling port was provided at a T joint following the gas meter. Gas flow from the meter was diluted with nitrogen prior to its discharge into the laboratory hood. A thermocouple was located in the second opening of the three neck flask and the intake to an FMI laboratory pump in the other. The pump was used to transfer liquid product from the flask to Teflon coated polyethylene storage bottles. All glass containers used to store or sample trimethoxysilane and triethoxysilane were washed with dilute HCl, rinsed thoroughly with methanol (or ethanol) and oven dried at 110°C . prior to use.

GENERAL ACTIVATION AND REACTION PROCEDURE

Typically, the 5.8 L reactor was charged with 2 kg solvent, 1 kg silicon, copper catalyst precursor ($\text{Cu}(\text{OH})_2$) and 0.6–0.9 g surface-active agent and sealed. According to equation (1), complete conversion of 1 kg silicon will require 3.43 kg methanol (4.93 kg ethanol) and produce 4.36 kg $\text{HSi}(\text{OCH}_3)_3$ (5.86 kg $\text{HSi}(\text{OC}_2\text{H}_5)_3$) and 873 L H_2 at 298K and 1 atmosphere. The slurry was agitated at ~ 900 rpm and nitrogen introduced as it was heated to 250°C . This temperature was maintained for 0.25–3 hr to permit thorough copper activation of the silicon particles before alcohol was introduced. Longer activation times, for example up to 12 hr, may be used if desired.

Hydrogen pretreatment of the copper-silicon slurry was sometimes employed. When used, hydrogen was injected at 150°C . through the alcohol sparger and its flow maintained for 30 minutes after the final temperature (250°C .) had been reached. The total H_2 flow was recorded.

Activation with a polyaromatic hydrocarbon solvent like THERMINOL® 59 is also effective. In practice, the copper (II) hydroxide and THERMINOL® 59 are heated to 180° – 250°C . for 0.5–1 hr, optionally in the presence of silicon. The solvent is separated from the copper-containing solids, which are then dispersed in another solvent like NALKYLENE® 550 L along with silicon to form a slurry for the Direct Synthesis.

During activation, gas flow from the reactor was vented through the four-way valve and not admitted to the distillation columns until just prior to the initiation of alcohol flow. Simultaneous with activation, the alcohol vaporizer was heated to $\sim 150^{\circ}\text{C}$. and the refrigerant circulated through the reflux condenser was cooled to -25°C . Alcohol flow to the reactor was initiated when gas chromatographic analysis of the effluent stream (24 in FIG. 1) showed that there was only nitrogen in the vent gas. Of course, comparative experiments (see Example ?) were run without the addition of a surface-active agent.

Once the alcohol flow was underway, sampling and analysis of the vent gas stream (24 in FIG. 1) for hydrogen were done every 10–15 minutes until a stable composition was established. That indicated the end of the induction period. Thereafter, gas sampling was done every 30 minutes to monitor hydrogen, hydrocarbons and ethers. During the course of the reaction, total vent gas flow was used as an approximate measure of the reaction rate according to the stoichiometry of equation (1).

Samples were collected in acid washed, alcohol rinsed, dried refrigerated containers attached at the four-way sam-

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pling valve (15 in FIG. 1) for 2–5 minutes every half hour. They were weighed and analyzed by gas chromatography. The bulk of the liquid product was condensed in the three neck flask which served as the reboiler (17 in FIG. 1) and transferred to storage. All of these data were used to calculate the temporal composition of the product stream, its selectivity to trialkoxysilane, the reaction rate and overall silicon conversion. Usually, reactions were terminated after >85% of the silicon charged to the reactor had been reacted. In some cases, terminations were made at lower and higher silicon conversions depending on the objective of the experiment.

Gas samples were analyzed for hydrogen, nitrogen and hydrocarbons (e.g. methane, ethane) content on a Hewlett Packard 5840 gas chromatograph fitted with a GS-Molesieve 30 m×0.53 mm internal diameter (J & W Scientific) capillary column and flame ionization detector. Argon was the carrier gas. Gas chromatography-mass spectrometry was used to analyze for dimethyl ether. Liquid samples containing alkoxysilanes were analyzed on a Hewlett Packard 5890 gas chromatograph with a 3.66 m×3.18 mm stainless steel column packed with 20% OV-101 on 60/80 mesh Chromosorb (Supelco).

Used solvent was analyzed by gravimetry and atomic absorption spectrometry for total silicon content and by ^{29}Si NMR for the speciation of the soluble silicon into Q^0 , Q^1 , Q^2 , Q^3 and Q^4 groups. The chemical shifts (relative to tetramethylsilane) of these functional groups are set forth below.

GROUP	STRUCTURE	^{29}Si NMR SHIFTS (ppm)
Q0	$\text{Si}(\text{OR})_4$	-78.3 to -78.5
Q1	$\text{O}-\text{Si}(\text{OR})_3$	-85.6 to -85.9
Q2	$\text{O}-\text{Si}(\text{OR})_2-\text{O}$	-93.6 to -93.9
Q3	$\text{O}-\text{Si}-\text{O}(\text{OR})\text{O}$	-102.0 to -102.6
Q4	SiOSi_4	-110

Molar percentages of these groups are calculated from the integration areas.

MATERIALS USED

Technical grade silicon samples utilized in the experiments of the illustrative Examples are listed in Table 1 along with relevant analytical data. Silicon samples used in Examples 1, 2, 3 and 5 satisfied the composition ranges and particle size distribution given below for Si-1. Silicon sample Si-2 was used in Example 4. All samples contained minimally 98.5 wt % Si. Table 2 presents a data summary for the copper hydroxide catalysts used. NALKYLENE® 550 BL, NALKYLENE® 600 L, THERMINOL® 59, THERMINOL® 66 and MARLOTHERM® S were the solvents used. FS 1265 (Dow Corning) and SAG® 100 (OSI Specialties) were the surface-active additives.

TABLE 1

COMPOSITION OF SILICON SAMPLES USED IN ILLUSTRATIVE EXAMPLES		
ELEMENT	SAMPLE Si-1	SAMPLE Si-2
Al, wt %	0.2–0.35	0.08
Ba, ppm	13.4	<3
Ca, ppm	130–517	600
Cr, ppm	25–100	58.9
Cu, ppm	19–50	34.8

TABLE 1-continued

Fe, wt %	0.25-0.65	0.38
Mg, ppm	20-100	8.8
Mn, ppm	100-300	90.4
Ni, ppm	<10	15.5
P, ppm	25-50	26.8
Pb, ppm	<10	<10
Sn, ppm	<10	<10
Ti, ppm	310-501	299
V, ppm	20-100	14.3
Zn, ppm	<10	<5
Zr, ppm	100-300	29
Si	Balance	Balance

PARTICLE SIZE DISTRIBUTION OF SILICON
SAMPLES USED IN ILLUSTRATIVE EXAMPLES

NOMINAL SIEVE SIZE, μ	Wt % > NOMINAL SIZE, Si-1	Wt % > NOMINAL SIZE, Si-2
600	0	3.1
425	0	14.0
300	1.6	18.7
250	28.4	13.7
180	30.3	11.9
75	39.5	24.1
<75	0.1	
45		1.5
<45		11.6

TABLE 2

CHARACTERIZATION OF COPPER (II)
HYDROXIDE CATALYST USED IN
ILLUSTRATIVE EXAMPLES

PROPERTY	VALUE
Cu, wt %	57.50-58.5
Al, ppm	250-1000
As, ppm	<30
Ca, wt %	0.11-0.22
Fe, ppm	120-2000
P, wt %	1.5-1.8
Pb, ppm	100-300
Sb, ppm	20-100
Sn, ppm	<50-100
Zn, wt %	0.03-0.2
H ₂ O, wt %	<1.0-10
Cl ⁻ , ppm	110-350
SO ₄ ²⁻ , wt %	0.5-3
Surface Area, m ² /g	20-40
Particle Size Range, μ	0.1-20

EXAMPLE 1

This Example illustrates the use of SAG® 100 compound as a defoamer and antifoam during the Direct Synthesis of HSi(OCH₃)₃.

The experiment was performed in the 3.8 L Chemineer® reactor with 1.4 kg THERMINOL® 66, 700 g silicon Si-1 and 4.6 g Cu(OH)₂. The slurry was stirred (800 rpm) and heated to 220° C. in the presence of flowing nitrogen to activate the silicon-copper solids for reaction. The level of the stirred slurry was ~75% of the height of the reactor. Methanol was introduced at 6 g/min after the reaction slurry had been at 220° C. for about 40 minutes. Temperatures recorded along the packed entrainment separator/partial distillation column attached to the exit of the reactor are set forth in Table 3. Thermocouple 1 (T1) was at the same level as the top of the reactor and thermocouple 5 (T5) was farthest away from it. Data are shown only for three of the five recording thermocouples.

When, after about 3.5 hr, the T1 temperature jumped from -122° C. to 181° C., it was apparent that hot reaction slurry had climbed to the top of the reactor. Reduction of the methanol flow rate to 4 g/min and even to 2 g/min after 4.5 hr and 5.5 hr, respectively, did not effect foam subsidence. T1 registered 199.6° C. at 5.8 hr, just prior to the injection of 0.5 g SAG@100 into the hot reaction slurry. That defoaming was practically instantaneous was indicated by the sudden temperature drop at T1 to 118°-120° C. Methanol flow was increased again to 6 g/min and the reaction was continued for another 2 hr with no further temperature jump at T1.

TABLE 3

TIME, hr	REACTOR TEMP. °C.	T1, °C.	T3, °C.	T5, °C.	NOTES
0	219	69.6	59.2	35	Start CH_3OH 6 g/min
0.75	219	126.2	83.6	75.4	
1.5	220	117.3	83.2	73.7	
2.0	220	121.7	83.1	72.9	
2.5	220	121.7	83.1	72.9	
3.5	222	181.0	80.8	70.3	Foaming CH_3OH
4.5	218	187.5	77.0	67.4	4 g/min
5.5	219	199.6	78.0	65.7	CH_3OH 2 g/min
5.8	220	199.6	85.1	65.7	0.5 g SAG @ 100
6.5	220	118.0	78.0	74.9	No Foaming
7.5	223	120.0	76.1	67.9	No Foaming

These data indicate that, in the absence of a foam control additive, foaming probability increases with reaction time. Soluble silicate concentrations in the reaction slurry increase with time and might contribute to foaming. SAG@ 100 effectively reduced or eliminated foam formation when it was added during the course of the reaction.

EXAMPLES 2A-C

This Example illustrates the reduction of the time to attain steady-state selectivities brought about by the addition of the surface-active additives, SAG@100 and FS 1265, to the reaction slurry at the outset of the Direct Synthesis.

Three reactions are summarized in this Example. Each was run in the 5.8 L Chemineer reactor at 250° C. and 800 rpm with a slurry containing 2.14 kg THERMINOL@ 59, 1.07 kg silicon Si-1, 7.06 g $\text{Cu}(\text{OH})_2$ and CH_3OH feed rate, 3 g/min. The stirred slurry level was ~50% of the total reactor height. Whereas Example 2A was run without the addition of surface-active agent, 0.64 g SAG@ 100 was added to the slurry of Example 2B and 0.64 g FS 1265 was added to the slurry of Example 2C at the outset of the experiments. All three slurries were activated thermally by heating to 250° C. in the presence of bubbling nitrogen. Temperature increases along the entrainment separator/partial distillation column similar to those reported in Example 1 were not observed in these experiments on account of the longer disengagement zone in 5.8 L reactor.

Reaction performance is summarized in Table 4. Table 4 shows that, in Example 2A, 5 hours elapsed before the experiment produced samples having approximately constant (~80-85 wt %) levels of $\text{HSi}(\text{OCH}_3)_3$. Stable (~85-88 wt %) values were already realized in the experiment of Example 2B within 2 hours. Three hours were required in

Example 2C to attain 79–83 wt %. Total weights of crude $\text{HSi}(\text{OCH}_3)_3$ in Examples 2B and 2C exceeded that in Example 2A by 100–200 g. These improvements were effected by 20 parts per million SAG® 100 or FS 1265 based on the total initial weight of the slurry.

TABLE 4

YIELD IMPROVEMENTS AND REDUCTION IN TIME TO STEADY-STATE SELECTIVITY CAUSED BY 20 ppm SAG ® 100 AND FS 1265 IN $\text{HSi}(\text{OCH}_3)_3$ DIRECT SYNTHESIS			
Surface-active Additive TIME, hr	EXAMPLE 2A None TMS, wt %	EXAMPLE 2B SAG ® 100 TMS, wt %	EXAMPLE 2C FS 1265 TMS, wt %
1	50.77	68.05	61.88
2	61.26	87.07	66.60
3	68.61	85.15	79.25
4	80.45	86.24	82.30
5	84.89	87.66	83.26
Total Weight of Crude Product, kg	1.03	1.23	1.14

EXAMPLES 3A–B

This Example illustrates that the fluorosiloxane, FS 1265, is an effective and durable antifoam in the Direct Synthesis of $\text{HSi}(\text{OCH}_3)_3$ when an alkylated benzene (N550BL) or mixture of diphenyl ethanes (TH59) is the reaction solvent and the reaction slurry is activated with hydrogen.

The slurry of Example 3A was prepared in the 5.8 L reactor with 1 kg silicon (Si-1), 2 kg N550BL, 7.05 g $\text{Cu}(\text{OH})_2$ and 0.6 g FS 1265. That of Example 3B contained 2 kg TH59 in place of N550BL. In each case, hydrogen was introduced when the temperature of the slurry was 150° C. and its flow maintained for 30 minutes after the temperature reached 250° C. Total hydrogen usage was 451.3 L in Example 3A and 1803.9 L in Example 3B. On a molar basis, these volumes far exceeded the 0.064 mole (1.56 L) required to reduce the 7.05 g copper catalyst charged to the reactor. This excess was necessary because of the larger mass and surface area of silicon particles relative to copper (II) hydroxide in the slurry.

A nitrogen sparge was used to eliminate hydrogen from the reactor before methanol was introduced. This was done so that only hydrogen produced as a result of the methanol-activated silicon reaction would be measured in the vent gas. Methanol flow was 3.3 g/min. Vent gas samples were analyzed by gas chromatography every 10–15 minutes following the start of methanol flow until the area ratio of hydrogen to nitrogen attained a stable value. H_2 =92 area %, N_2 =8 area % was observed within 90 minutes and remained within ± 0.5 area % of these values for greater than 23 hr in both experiments. The slurries remained contained within the reactor during the course of both reactions. There was no visible or temperature indication of foaming.

92–94 wt % of the silicon charged was converted to crude reaction product in both Examples. The reaction of Example 3A produced a total of 4.8 kg crude product containing 3.78 kg $\text{HSi}(\text{OCH}_3)_3$ and 0.31 kg $\text{Si}(\text{OCH}_3)_4$, while that of Example 3B produced 5.3 kg crude containing 3.93 kg $\text{HSi}(\text{OCH}_3)_3$ and 0.13 kg $\text{Si}(\text{OCH}_3)_4$. Soluble silicon in the spent slurry of Example 3A was 0.5 wt %. ^{29}Si NMR disclosed the following speciation of silicate groups: Q^0 =3.3 mole %, Q^1 =62.8 mole %, Q^2 =33.9 mole %. The spent slurry of Example 3B contained 0.16 wt % soluble silicon and had very weak ^{29}Si NMR signals.

EXAMPLE 4

This Example illustrates the Direct Synthesis of $\text{HSi}(\text{OC}_2\text{H}_5)_3$ in the solvent MARLOTHERM® S with and without the fluorosiloxane, FS 1265. The hydrogen activated slurries of both experiments were initially reacted with methanol before the reactions were continued with ethanol.

In Example 4A, the reaction slurry contained 0.8 g FS 1265. No surface-active agent was intentionally added to the experiment of Example 4B. Otherwise, each of the two experiments of this Example was conducted with 1 kg silicon (Si-2), 14.1 g $\text{Cu}(\text{OH})_2$ and 2.1 kg MARLOTHERM® S. Each slurry was activated with hydrogen as described in the general procedure above. A total of 1403.8 L H_2 was introduced in Example 4A and 1259 L H_2 in Example 4B between 150°–250° C. over a period of 65 minutes. With the temperature at 250° C. in both experiments, methanol was introduced at 4.3 g/min and its flow maintained for 5 hours. In that time, ~20% silicon was converted primarily to $\text{HSi}(\text{OCH}_3)_3$ and $\text{Si}(\text{OCH}_3)_4$.

After the reactor temperature had been lowered and stabilized at 230° C., ethanol was introduced at 4.3 g/min. Nitrogen flow was maintained during the temperature drop. No H_2 was present in the vent gas just prior to the start of the ethanol feed. Vent gas analysis 10–15 minutes after the initiation of ethanol flow showed the presence of H_2 . In Example 4A, gas chromatographic analysis of the vent gave stable values of H_2 =85 area % , N_2 =15 area % and in Example 4B H_2 =76 area % , N_2 =24 area % after about 30 minutes.

The liquid reaction products were analyzed periodically for $\text{HSi}(\text{OC}_2\text{H}_5)_3$, $\text{Si}(\text{OC}_2\text{H}_5)_4$ and other byproducts. That from Example 4A contained ~80 wt % $\text{HSi}(\text{OC}_2\text{H}_5)_3$, ~20 wt % $\text{C}_2\text{H}_5\text{OH}$ and a trace of $\text{Si}(\text{OC}_2\text{H}_5)_4$ after 60 minutes. Trialkoxysilane yield was 558 g $\text{HSi}(\text{OC}_2\text{H}_5)_3$ within 4.5 hr. In contrast, liquid product from the experiment of Example 4B contained ~60 wt % $\text{HSi}(\text{OC}_2\text{H}_5)_3$ and ~40 wt % $\text{C}_2\text{H}_5\text{OH}$ after 60 minutes. The reaction produced 380.5 g $\text{HSi}(\text{OC}_2\text{H}_5)_3$ in 4.5 hr.

The higher content of H_2 in the vent gas of the experiment of Example 4A was indicative of a higher $\text{HSi}(\text{OC}_2\text{H}_5)_3$ production rate brought about by the presence of the fluorosilicone in the reaction slurry. Although, both reactions attained steady-state in about 30 minutes, the slurry containing FS 1265 was producing 20 wt % more $\text{HSi}(\text{OC}_2\text{H}_5)_3$ than the one without this surface-active additive.

EXAMPLE 5

This Example illustrates the occurrence and control of foaming during the Direct Synthesis of $\text{HSi}(\text{OCH}_3)_3$ in the 400 L stainless steel pilot scale reactor at 250° C. and 400 rpm.

The reactor was charged with 136 kg THERMINOL® 59, 68 kg silicon (Si-1), 0.45 kg $\text{Cu}(\text{OH})_2$ and 231 kg methanol. This mixture was slurried at 400 rpm and heated to 250° C. with a nitrogen sparge. This thermal activation was continued for 3.25 hr. Thereafter, methanol flow was initiated at 7.7 kg/hr and increased in stages up to 11.8 kg/hr. Foam formation was monitored visually through the observation window at the top of the reactor.

With fresh THERMINOL® 59, or that which had been treated for removal of soluble silicates by the process of U.S. Pat. No. 5,166,384, foaming was initially not observed even at the highest methanol flow rates. When the THERMINOL® 59 had been used in previous reactions and the soluble silicates had not been removed, foaming was some-

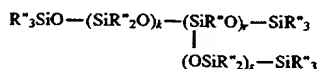
times observed even at the lowest (7.7 kg/hr) methanol flow rate. In most cases, there was no carryover of foam into the distillation columns because the reactor was designed with a long disengagement height.

In one experiment with a previously used batch of solvent which had been centrifuged at 1000 rpm for particulate separation, but not chemically treated for soluble silicate removal, foaming was visible when the methanol flow rate was increased from 7.7 kg/hr to 9.1 kg/hr. A solution containing 66 g FS 1265 in 594 g THERMINOL® 59 was then injected into the reactor and the response observed through the observation window. Defoaming was instantaneous and vapors were observed to rise from the surface of the slurry to the reactor outlet. No additional foaming occurred during the ensuing hours of reaction at methanol flow rates of 9.1–11.8 kg/hr. The quantity of FS 1265 used was equivalent to 322 parts per million based on the total weight of slurry. Untreated solvent from this experiment was recycled, without further purification, to the reaction of three additional 68 kg batches of silicon. Foaming was not observed in any of these runs. Subsequent experiments showed that FS 1265 concentrations as low as 50, 100 and 200 parts per million can provide effective and durable defoaming action in the 400 L reactor.

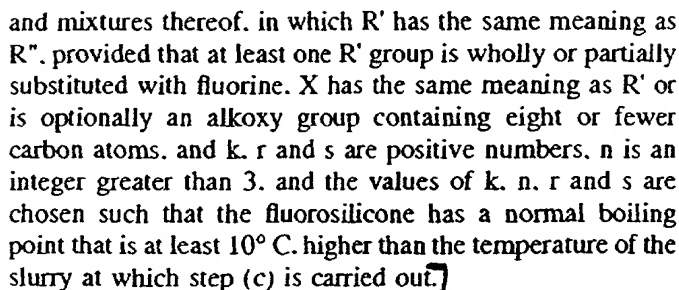
What is claimed is:

1. A process for producing trialkoxysilane of the formula $\text{HSi}(\text{OR})_3$ wherein R is an alkyl group containing 1 to 6 carbon atoms inclusive, comprising

- (a) slurring silicon metal in a thermally stable solvent in the presence of a surface-active additive and of a catalyst precursor which is halogen-free and which comprises copper,
- (b) activating said catalyst precursor, thereby generating a catalyst for the reaction of step (c), and
- (c) reacting said silicon metal with an alcohol of the formula ROH in the presence of the catalyst generated in step (b) to form said trialkoxysilane; wherein said surface-active additive comprises (i) a mixture of (i)(A) hydrophobized silica particles with average particle sizes in the range of 0.2–5 microns, and specific surface area between 50 and 400 square meters per gram and (i)(B) an organopolysiloxane selected from the group consisting of compounds of the general formula: $\text{R}^*_3\text{SiO}-(\text{SiR}^*_2\text{O})_n-\text{SiR}^*_3$, cyclic compounds of the general formula: $(\text{R}^*_2\text{SiO})_n$, branched oligomers and polymers of the formula



and mixtures thereof, wherein R* in each occurrence is the same or different and each is a C₁–C₂₀ alkyl group, phenyl, alkyl-substituted phenyl, cycloalkyl, or alkyl-substituted cycloalkyl; a, b, k, r and s are greater than zero and have values such that the normal boiling point of the organopolysiloxane is at least 10° C. higher than the temperature of the Direct Synthesis slurry; wherein the weight ratio of (i)(A) to (i)(B) is 1:99 to 99:1, or (ii) an organofluorosiloxane selected from the group consisting of compounds of the general formula $\text{XR}'_2\text{SiO}-(\text{SiR}'_2\text{O})_n-\text{SiR}'_2\text{X}$, cyclic compounds of the general formula $(\text{R}'_2\text{SiO})_n$, branched oligomers and polymers of the formula



2. The process of claim 1 wherein R is methyl.
3. The process of claim 1 wherein R is ethyl.
4. The process of claim 1 wherein said catalyst precursor comprises one or more copper(I) compounds.
5. The process of claim 1 wherein said catalyst precursor comprises one or more copper(II) compounds.
6. The process of claim 1 wherein said catalyst precursor comprises copper(II) hydroxide.
7. The process of claim 1 wherein the slurry formed in step (a) contains alcohol of the formula ROH.
8. The process of claim 1 wherein in step (a) said solvent comprises polyaromatic hydrocarbons, and said catalyst precursor is activated in step (b) by heating in said solvent, and said step (c) is carried out in a solvent comprising alkylated benzene.

[1]

10. The process of claim 9 wherein step (b) is carried out by reacting said catalyst precursor with gaseous hydrogen.

11. The process of claim 9 wherein step (b) is carried out by reacting said catalyst precursor with carbon monoxide.

12. The process of claim 9 wherein step (b) is carried out by reacting said catalyst precursor with SiH_4 .

13. The process of claim 9 wherein step (b) is carried out by reacting said catalyst precursor with an organosilane containing one or more SiH groups.

14. The process of claim 9 wherein step (b) is carried out by reacting said catalyst precursor with an organosilane containing one or more SiH₃ groups.

15. The process of claim 9 wherein step (b) is carried out by reacting said catalyst precursor with an organosilane containing one or more SiH_3 groups.

16. The process of claim 9 wherein the slurry formed in step (a) contains alcohol of the formula ROH.

17. The process of claim 9 wherein hydrogen is formed in the reaction of step (c) and all or a portion of said hydrogen is recycled to step (b) and is used in the reduction of step (b).

18. The process of claim 9 wherein in step (a) said solvent comprises polyaromatic hydrocarbons, and said catalyst precursor is reduced in step (b) by heating in said solvent, and said step (c) is carried out in a solvent comprising alkylated benzene.

19. A process for producing trialkoxysilanes of the formula $\text{HSi}(\text{OR})_3$, wherein R is an alkyl group containing 1 to 6 carbon atoms inclusive, comprising the steps of:

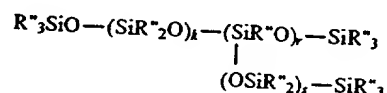
(a) slurrying silicon metal in a solvent in the presence of a surface-active additive and of a catalyst precursor which comprises copper;

(b) activating said catalyst precursor, thereby generating a catalyst for the reaction of step (c); and

(c) reacting said silicon metal with one or more alcohols of the formula ROH in the presence of the catalyst generated in step (b) to form said trialkoxysilanes;

wherein said surface-active additive comprises hydrophobized solid particles and

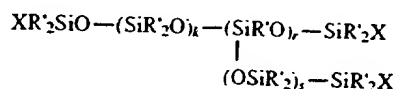
(i) an organopolysiloxane selected from the group consisting of compounds of the general formula $\text{R}''_3\text{SiO}-(\text{SiR}''_2\text{O})_k-\text{SiR}''_3$, cyclic compounds of the general formula $(\text{R}''_2\text{SiO})_n$ branched oligomers and polymers of the formula



and mixtures thereof, wherein R'' in each occurrence is the same or different and each is a C_1 - C_{20} alkyl group, phenyl, alkyl-substituted phenyl, cycloalkyl, or alkyl-substituted cycloalkyl; a, b, k, r and s are greater than zero and have values such that the organopolysiloxane has a normal boiling point that is at least 10°C higher than the temperature of the slurry during the reaction of step (c);

or

(ii) an organofluorosiloxane selected from the group consisting of compounds of the general formula $\text{XR}'_2\text{SiO}-(\text{SiR}'_2\text{O})_k-\text{SiR}'_2\text{X}$, cyclic compounds of the general formula $(\text{R}'_2\text{SiO})_n$ branched oligomers and polymers of the formula



and mixtures thereof, wherein R' in each occurrence is the same or different and has the same meaning as R'' provided that at least on R' group is wholly or partially substituted with fluorine, X has the same meaning as R' or is optionally an alkoxy group containing eight or fewer carbon atoms, and k, r, and s are positive numbers, n is an integer greater than 3, and the values of k, n, r and s are chosen such that the organofluorosiloxane has a

20. The process of claim 19, wherein the hydrophobized solid particles are silica.

22. The process of claim 19, wherein hydrophobized solid particles have an average particle size in the range of 0.2-5 microns.

23. The process of claim 19, wherein hydrophobized solid particles have a specific surface area between 50 and 400 square meters per gram.

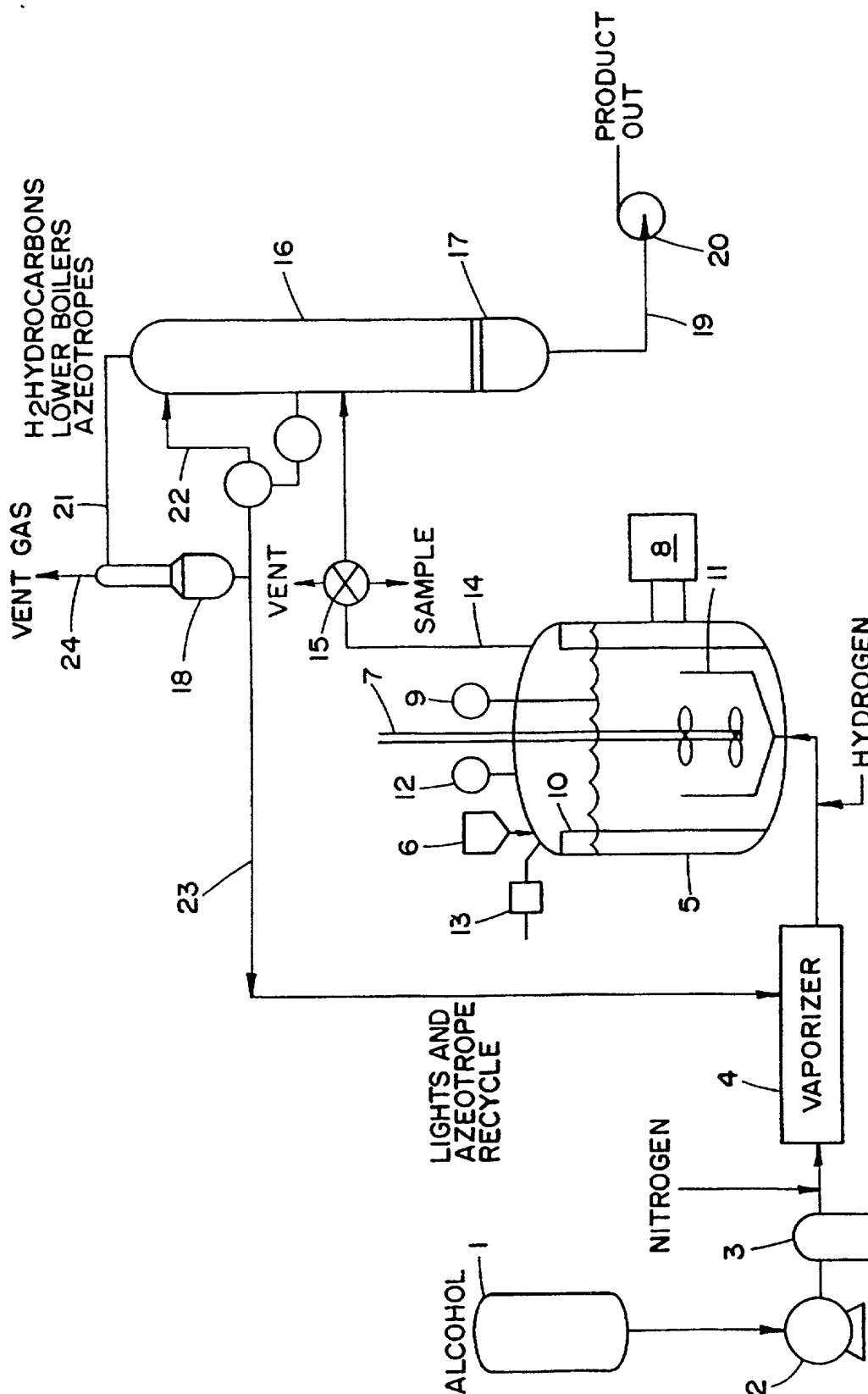


FIG. 1

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DECLARATION AND POWER OF ATTORNEY FOR REISSUE APPLICATION

We, Frank D. Mendicino, Kenrick M. Lewis, and Thomas E. Childress, hereby declare that we are citizens of the United States, and I, Hua Yu, , declare that I am a citizen of the People's Republic of China, and I, Sebastiano Magri, declare that I am a citizen of Italy, and we all (hereafter "we") declare that our residences are as stated below next to our names. We believe that we are the original and only inventors of the invention entitled SURFACE-ACTIVE ADDITIVES IN THE DIRECT-SYNTHESIS OF TRIALKOXY-SILANES described and claimed in our original application No. 08/729,266, filed October 10, 1996, and the resulting United States Patent No. 5,783,720 which issued July 21, 1998 ("the '720 patent"), and for which invention a reissue patent is solicited.

We do not know and do not believe that the invention of the '720 patent was ever known or used in the United States before our invention thereof. Furthermore, we do not know and do not believe that the invention was patented or described in any publication in any country before our invention thereof, or more than one year prior to the original application. We do not know and do not believe that the invention was in public use or on sale in the United States more than one year prior to the original application. To the best of our knowledge and belief, this invention has not been patented or made the subject of an inventors' certificate in any country foreign to the United States prior to the date of the original application on an application filed by us or our legal representatives or assigns more than 12 months before the original application.

We have reviewed and understand the contents of the attached specification, including the

claims, as amended by any amendments specifically referred to in this Declaration. We acknowledge the duty to disclose information of which we are aware and which is material to the examination of the application in accordance with 37 C.F.R. §§ 1.56(a) and 1.175(a) (7).

We believe that through error, without any deceptive intent, the '720 patent is partially inoperative or invalid by reason of the patentee claiming more or less than the patentee had the right to claim in the patent. In particular, there is a possible defect in independent claim 1 as issued, in that it is unduly narrow and not commensurate in scope with the description in the specification and what we believe our invention to encompass. Because it is unduly narrow, it may impact the scope of all other claims 2-18 which depend directly or indirectly on one of claim 1.

This possible error in the claim language arose without deceptive intent during prosecution of the application before the United States Patent and Trademark Office. Upon reviewing the issued claims in September 1999 we realized that the language of claims 1-18 could be clarified.

Therefore, by reason of the above-described errors, claims presented in original Patent 5,783,720 are possibly not broad enough to cover all aspects of the invention disclosed in the patent. The possible unduly narrow scope of the claims resulted from a failure by ourselves, the assignee and counsel to realize that the claims did not cover all that was intended to be covered as set forth in the specification. By this reissue application, the identified errors are believed to be corrected.

All errors which are being corrected in the present reissue application up of the time of filing of this declaration arose without any deceptive intention on the part of the applicant.

Date Signed: Dec. 7, 1999

Date Signed: _____

Date Signed: Dec. 1, 1993

Mendicino Reissue Application of U.S. Patent 5,783,720

Inventor's Name: Thomas E. Childress

Inventor's Residence: Route 1
Newport, Ohio 45768

Inventor's Citizenship: U.S.A.

Inventor's Signature: Thomas E. Childress

Date Signed: Dec 7, 1999

DECLARATION AND POWER OF ATTORNEY FOR REISSUE APPLICATION

We, Frank D. Mendicino, Kenrick M. Lewis, and Thomas E. Childress, hereby declare that we are citizens of the United States, and I, Hua Yu, , declare that I am a citizen of the People's Republic of China, and I, Sebastiano Magri, declare that I am a citizen of Italy, and we all (hereafter "we") declare that our residences are as stated below next to our names. We believe that we are the original and only inventors of the invention entitled SURFACE-ACTIVE ADDITIVES IN THE DIRECT-SYNTHESIS OF TRIALKOXYSILANES described and claimed in our original application No. 08/729,266, filed October 10, 1996, and the resulting United States Patent No. 5,783,720 which issued July 21, 1998 ("the '720 patent"), and for which invention a reissue patent is solicited.

We do not know and do not believe that the invention of the '720 patent was ever known or used in the United States before our invention thereof. Furthermore, we do not know and do not believe that the invention was patented or described in any publication in any country before our invention thereof, or more than one year prior to the original application. We do not know and do not believe that the invention was in public use or on sale in the United States more than one year prior to the original application. To the best of our knowledge and belief, this invention has not been patented or made the subject of an inventors' certificate in any country foreign to the United States prior to the date of the original application on an application filed by us or our legal representatives or assigns more than 12 months before the original application.

We have reviewed and understand the contents of the attached specification, including the

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claims, as amended by any amendments specifically referred to in this Declaration. We acknowledge the duty to disclose information of which we are aware and which is material to the examination of the application in accordance with 37 C.F.R. §§ 1.56(a) and 1.175(a) (7).

We believe that through error, without any deceptive intent, the '720 patent is partially inoperative or invalid by reason of the patentee claiming more or less than the patentee had the right to claim in the patent. In particular, there is a possible defect in independent claim 1 as issued, in that it is unduly narrow and not commensurate in scope with the description in the specification and what we believe our invention to encompass. Because it is unduly narrow, it may impact the scope of all other claims 2-18 which depend directly or indirectly on one of claim 1.

This possible error in the claim language arose without deceptive intent during prosecution of the application before the United States Patent and Trademark Office. Upon reviewing the issued claims in September 1999 we realized that the language of claims 1-18 could be clarified.

Therefore, by reason of the above-described errors, claims presented in original Patent 5,783,720 are possibly not broad enough to cover all aspects of the invention disclosed in the patent. The possible unduly narrow scope of the claims resulted from a failure by ourselves, the assignee and counsel to realize that the claims did not cover all that was intended to be covered as set forth in the specification. By this reissue application, the identified errors are believed to be corrected.

All errors which are being corrected in the present reissue application up of the time of filing of this declaration arose without any deceptive intention on the part of the applicant.

Wherefore we request that we may be allowed to surrender, and we hereby offer to surrender, said U.S. Letters Patent No. 5,783,720, and request that Letters Patent be reissued to ourselves and the assignee, CKWitco Corporation., for the same invention upon the foregoing amended reissue application.

We hereby declare further that all statements made herein of our knowledge are true and that all statements made on information and belief are believed to be true. We further declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

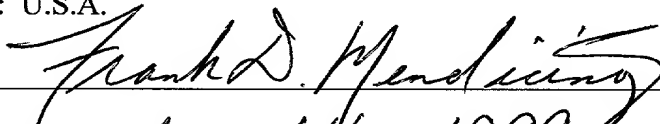
We hereby appoint Marlana K. Titus (Reg. No. 35,843) and Caroline Nash (Reg. No. 36,329) of Nash & Titus, LLC, 3415 Brookeville Road, Suite 1000, Brookeville, Maryland 20833, (301) 924-9600 (to whom all communications are to be directed) individually and collectively as our attorneys to prosecute this application and to transact all business in the Patent and Trademark office connected therewith and with the resultant Patent.

Inventor's Name: Frank D. Mendicino

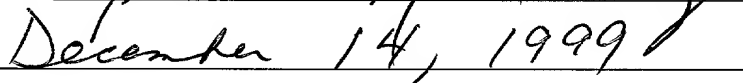
Inventor's Residence: 111 Heiss Drive
Marietta, Ohio 45750

Inventor's Citizenship: U.S.A.

Inventor's Signature:



Date Signed:



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**Inventor's Residence: 98-40 57th Avenue, #9M
Rego Park, New York 11368**

Inventor's Signature: _____

Date Signed: _____

Inventor's Residence: Via Asia 55
83039 Termoli (CB)
Italy

Inventor's Signature: Sebastiano Negro

Date Signed: 12/11/99

Inventor's Residence: 12-17 Granada Crescent
White Plains, New York 10603

Inventor's Signature: _____

Date Signed: _____

Mendicino Reissue Application of U.S. Patent 5,783,720

Inventor's Name: Thomas E. Childress

Inventor's Residence: Route 1
Newport, Ohio 45768

Inventor's Citizenship: U.S.A.

Inventor's Signature: _____

Date Signed: _____